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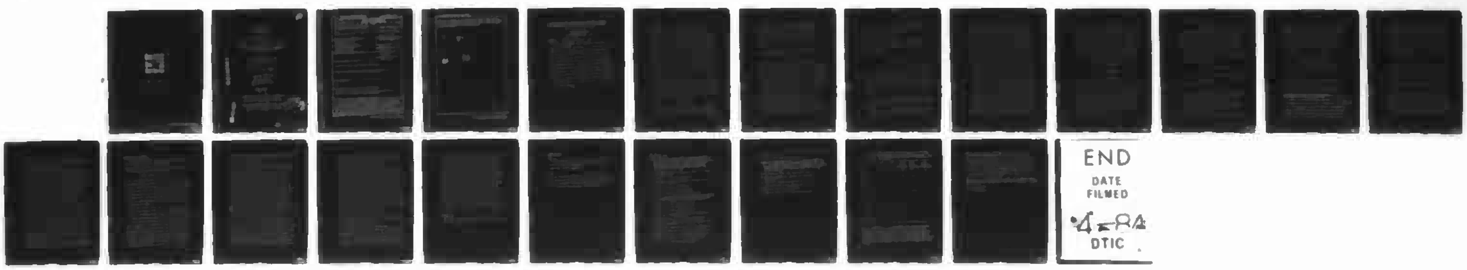

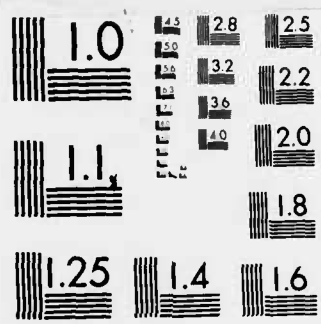

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The Influence of Specific Reactant-Solvent Interactions on Intrinsic Activation Entropies for Outer-Sphere Electron Transfer Reactions

by

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THE INFLUENCE OF SPECIFIC REACTANT-SOLVENT INTERACTIONS ON INTRINSIC ACTIVATION ENTROPIES FOR OUTER-SPHERE ELECTRON TRANSFER REACTIONS.

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ABSTRACT

The physical basis of the solvent contribution to the intrinsic activation entropy, ΔS^*_{int}, for outer-sphere electron-transfer reactions in homogeneous solution is examined in terms of the entropic parameters for the constituent electrochemical half reactions. A relationship for calculating ΔS^*_{int} is derived which takes into account specific reactant-solvent interactions for the isolated redox centers by employing electrochemical reaction entropy data. This relation yields rather larger and more structure-sensitive values of ΔS^*_{int} than those deduced on the basis of the usual dielectric continuum treatment. These considerations indicate that the more negative values of ΔS^*_{int} typically extracted from experimental kinetic data arise largely from the modification to the specific reactant-solvent interactions within the precursor complex caused by the proximity of the other redox center.

INTRODUCTION

In recent years increasingly detailed and sophisticated theories of outer-sphere electron-transfer kinetics have been formulated.[1] These enable rates and activation parameters to be calculated from reaction thermodynamics together with reactant and solvent structural information. Although treatments of inner-shell (intramolecular reactant) reorganization have reached a high degree of sophistication,[2] the important contribution to the free energy barrier arising from outer-shell (noncoordinated solvent) reorganization is usually treated in terms of the classical dielectric continuum model as originally formulated by Marcus.[3] While comparisons between theory and experiment for bimolecular outer-sphere processes show reasonable agreement in a number of cases, significant and often large discrepancies still remain.[4,5] Among other things, such discrepancies call into question the quantitative validity of the dielectric continuum model, especially in view of the well-known failure of similar treatments to describe the thermodynamics of ion solvation.

In principle, a useful way of monitoring the influence of outer-shell solvation upon electron-transfer energetics is to evaluate entropic parameters since these are expected to arise chiefly from the changes in the degree of solvent polarization associated with electron transfer. The activation entropy, ΔS^*, as for other reorganization parameters, can usefully be divided into "intrinsic" and "thermodynamic" factors:[6,7]

$$\Delta S^* = \Delta S^*_{int} + \beta\Delta S^\circ \qquad (1)$$

where the coefficient β is predicted to usually be close to 0.5.[8] The intrinsic activation entropy, ΔS^*_{int}, is that component of ΔS^* that remains in the absence of the entropic driving force ΔS°. When estimating values

of ΔS^* from Eq (1), it is usual to employ experimental values of $\Delta S°$ and yet values of ΔS^*_{int} calculated from dielectric continuum theory. Although these calculated values of ΔS^*_{int} are often small, given that the values of $\Delta S°$ are often much larger and more variable than those calculated from the dielectric continuum model, it is reasonable to inquire if a more trustworthy method for estimating ΔS^*_{int} could be formulated.

A useful and often enlightening approach for understanding electron transfer processes both on a conceptual and an experimental basis is to examine the thermodynamics and kinetics of electrochemical reactions:[9-13]

$$\mathrm{Ox} + e^-(\phi_m) \rightleftarrows \mathrm{Red} \qquad (2)$$

where ϕ_m is the (Galvani) electrode-solution potential difference. Although absolute values of ϕ_m cannot be evaluated with useful accuracy, the temperature dependence of ϕ_m can be obtained using a nonisothermal cell arrangement.[10,12] This enables the entropic change induced by reduction of a single redox center, the so-called "reaction entropy" ΔS°_{rc}, to be determined from the temperature dependence of the standard (or formal) potential ϕ^o_m under these conditions.[12] Activation parameters for such electrochemical "half reactions" can be obtained using an analogous procedure.[9,10] These quantities provide insights into the structural changes accompanying electron transfer at each redox center that remain hidden for homogeneous bimolecular reactions.

The aim of this communication is first to provide a simple physical picture, based on electrochemical half-reactions, of the origin of the intrinsic activation entropy in homogeneous and electrochemical redox reactions. With this background a new approach for estimating ΔS^*_{int} will be outlined based on reaction entropy data whereby the effects of specific

reactant-solvent interactions can be taken into account. Despite their potential importance, such interactions have yet to be considered even in the more sophisticated theories of electron transfer.

Origin of the Intrinsic Activation Entropy

The actual entropic barriers, ΔS_f^* and ΔS_r^*, to electron transfer for the forward (reduction) and reverse (oxidation) electrochemical reactions at a given electrode potential have been termed "ideal" activation entropies.[9-11] These can be formulated as

$$\Delta S_f^* = \alpha\Delta S_{rc}^\circ + \Delta S_{int,e}^* \qquad (3a)$$

$$\Delta S_r^* = (\alpha-1)\, \Delta S_{rc}^\circ + \Delta S_{int,e}^* \qquad (3b)$$

where α is the electrochemical transfer coefficient and $\Delta S_{int,e}^*$ is the so-called "real" (or intrinsic) electrochemical activation entropy, i.e. that which remains after accounting for the entropic driving force.[9] For convenience, we shall assume that the interactions between the reactant and electrode, and between the reactant pair in homogeneous solution, are weak and nonspecific (i.e. the "weak interaction" limit).[13] Under these circumstances $\Delta S_{int,e}^*$ is related to the intrinsic activation entropy for the corresponding self-exchange reaction by

$$\Delta S_{int}^* = 2\Delta S_{int,e}^* \qquad (4)$$

Relationships such as Eq. (4) reflect the fact that homogeneous outer-sphere reactions can be regarded as coupled reductive and oxidative electrochemical reactions.

Equations (3a) and (3b) point to a key difference between homogeneous self-exchange and electrochemical exchange reactions: the latter are

characterized by a net entropy driving force ΔS°_{rc} even when the free energy driving force is zero. This results from the inherent chemical asymmetry of the electrochemical half reactions. This entropy driving force contributes to the forward or reverse entropic barrier for each redox center to an extent determined by the difference in (hypothetical) charge between the oxidized or reduced reactant and the transition state, namely α or $(\alpha-1)$. The transition state of course never acquires a fractional charge since electron transfer occurs much more rapidly than nuclear motion, but nonetheless is characterized by a polarized solvent environment appropriate to a molecule possessing such a charge.[1,3]

According to the theoretical approach of Marcus[3], solvent reorganization to form the transition state can be viewed as occurring by a hypothetical two-step process.[1a,14] First the charge of the reactant is slowly adjusted to a fractional charge approximately midway between the reactant and product charges, with attendant reorientation of the surrounding solvent. Then in a rapid step (much faster than solvent motion) the transition-state charge is reset to that of the reactant. Taken together, the energies of the two steps are equivalent to the non-equilibrium solvent polarization energy. On the basis of the conventional dielectric continuum approach, the energetics of the first step are determined by the static solvent dielectric constant ε_s, while the optical (i.e. infinite frequency) dielectric constant ε_{op} determines the energy of the fast second step. We shall term these two steps the "static" and "optical" components, respectively. Generally the optical component is anticipated to provide the dominant contribution to the free energy of solvent reorganization due to the relative magnitudes of ε_{op} and ε_s. However, the temperature coefficients of the two dielectric constants are such that in many solvents the optical and static components are calculated to contribute

roughly equally to the entropic component of the solvent barrier.

The conventional calculation of the solvent reorganization energetics involves an application of the Born ion solvation model to transition state theory.[1a,14] The Born model predicts that entropies of ions will vary with the square of the charge number.[15] It is reasonable to suppose that the static component of the electrochemical transition-state entropy will also depend on the square of the effective charge. The differences in static entropy between the transition and ground states should be appropriately weighted fractions of the total entropy difference ΔS°_{rc} between the two ground redox states. We can therefore express the static components of the forward and reverse electrochemical activation entropies as

$$\Delta S^*_f(\text{static}) = \frac{[(n+1)^2-(n+1-\alpha)^2]}{[(n+1)^2-n^2]} \Delta S^\circ_{rc} \qquad (5a)$$

$$\Delta S^*_r(\text{static}) = \frac{[n^2-(n+1-\alpha)^2]}{[(n+1)^2-n^2]} \Delta S^\circ_{rc} \qquad (5b)$$

where n and n+1 are the charge numbers of the two forms of the redox couple, and (n+1-α) is the effective transition-state charge.

It can be seen from Eqs.(5a) and (5b) that even for a transition state that is symmetrical with respect to charge, i.e. $\alpha = 0.5$, that $\Delta S^*_f(\text{static})$ will differ from $-\Delta S^*_r(\text{static})$. In other words, the transition state will not lie midway in terms of entropy between the reduced and oxidized states even though it may be equally accessible in terms of free energy from either oxidation state. This mismatch of the energetics of the forward and reverse half reactions follows from the *linear* variation of driving force contributions with charge (Eq.(3)), coupled with the *quadratic* dependence of static entropy on charge.

Equations (3a) and (3b) can be combined to yield

$$\Delta S^*_{int,e} = (1-\alpha)\Delta S^*_f + \alpha\Delta S^*_r \qquad (6)$$

The intrinsic activation entropy therefore is a measure of the extent of the mismatch between forward and reverse half-reaction entropic barriers after normalizing for driving force contributions. This is seen most clearly when $\alpha = 0.5$ and the driving force components of ΔS^*_f and ΔS^*_f exactly cancel. The connections between the various entropic quantities are illustrated schematically in Fig. 1. The magnitude of ΔS^*_{int} is given by the vertical displacement of the curve AB, describing the dependence of the entropy upon the effective ionic charge, from the chord to this curve shown as a dashed line.

Equations 5a and 5b can be combined with Eq. 6 to yield an expression for the static component of $\Delta S^*_{int,e}$:

$$\Delta S^*_{int,e}(\text{static}) = \frac{\alpha\,(1-\alpha)}{2n+1}\,\Delta S^\circ_{rc} \qquad (7)$$

Taking $\alpha = 0.5$ and inserting the Bornian expression for the reaction entropy:[16]

$$\Delta S^\circ_{rc} = -\frac{Ne^2}{2r\varepsilon_s^2}\left(\frac{d\varepsilon_s}{dT}\right)\left[(n+1)^2-n^2\right] \qquad (8)$$

into Eq. (7) yields:

$$\Delta S^*_{int,e}(\text{static}) = -(Ne^2/8r\varepsilon_s^2)\,(d\varepsilon_s/dT) \qquad (9)$$

where N is the Avogadro number, e is the electronic charge, and r is the reactant radius. Note that the apparent dependence of $\Delta S^*_{int,e}$(static) on reactant charge (Eq. (7)) has now been eliminated.

Equation (8) can be compared with the relation obtained from the temperature derivative of the usual dielectric continuum expression for the reorganization free energy:[3,10]

$$\Delta S^*_{int,e} = [(Ne^2/8)(1/r - 1/R)]\,[(1/\varepsilon_{op}^2)\,(d\varepsilon_{op}/dT)-(1/\varepsilon_s^2)(d\varepsilon_s/dT)] \qquad (10)$$

Equations (9) and (10) differ in that the latter takes account of image stabilization of the ion in the vicinity of the electrode by including the ion-image separation distance R; furthermore, the optical portion of the activation entropy is included. This term is similar in form to the static term since it is assumed, based on linear response of solvent polarization to the field of the ion, that the optical portion of $\Delta S^*_{int,e}$ also varies with the square of the effective charge of the transition state.[1b]

Similarly, from Eqs. (4) and (7) the static portion of the intrinsic entropy for homogeneous self-exchange reactions can be expressed as

$$\Delta S^*_{int}(\text{static}) = \frac{2\alpha(1-\alpha)}{2n+1} \Delta S^\circ_{rc} \qquad (11)$$

Again, for $\alpha = 0.5$ and on the basis of the Bornian model [Eq. 8], this leads to

$$\Delta S^*_{int}(\text{static}) = (Ne^2/4r\varepsilon_s^2)\ (d\varepsilon_s/dT)] \qquad (12)$$

This is identical in form to the dielectric continuum expression for ΔS^*_{int} [cf Eq (10)]:

$$\Delta S^*_{int} = (Ne^2/4)\ (\frac{1}{r} - \frac{1}{R_h})\ [(1/\varepsilon_{op}^2)\ (d\varepsilon_{op}/dT)-(1/\varepsilon_s^2)(d\varepsilon_s/dT)] \qquad (13)$$

allowing again for the addition of the optical term and the presence of the nearby coreactant through the internuclear distance term R_h.

<u>Real Chemical Environments. Incorporating Specific Reactant-Solvent Interactions in Activation Entropy Calculations.</u>

In general, the experimental values of ΔS°_{rc} differ widely from the continuum predictions of Eq. (8). In water, for example, ΔS°_{rc} for the $Cr(H_2O)_6^{3+/2+}$ couple is seven times greater than predicted, while the experimental value of ΔS°_{rc} for $Fe(bpy)_3^{3+/2+}$ is less than a third of the theoretical value.[12] Furthermore, the expected variation of reaction entropies with solvent dielectric properties is not observed.[16-18] The discrepancies between theory

and experiment have variously been attributed to dielectric saturation, hydrogen bonding between reactants and solvent,[12] long range solvent structuring,[16-19] and hydrophobic interactions[20]. Consequently, in view of Eq.(11) dielectric continuum theories of solvent reorganization are not expected to provide accurate estimates of intrinsic activation entropies.

Nevertheless Eq.(11) suggests a means of incorporating the numerous factors neglected in the dielectric continuum treatments. Rather than employing estimates of ΔS°_{rc} based on Eq.(8), experimental values of ΔS°_{rc} can be used to determine the static component of ΔS^*_{int}. Therefore instead of Eq. (13) the intrinsic activation entropy can be expressed as

$$\Delta S^*_{int} = (Ne^2/4)\ (\frac{1}{r} - \frac{1}{R_h})\ [(1/\varepsilon^2_{op})\ (d\varepsilon_{op}/dT)] + \Delta S^\circ_{rc}/(4n + 2) \qquad (14)$$

The optical component of ΔS^*_{int}, the first term on the r.h.s. of Eq. (14), is unchanged from Eq. (13); however the static component embodied in the second term is taken instead from Eq. (11) with $\alpha = 0.5$ (As expected, α is commonly observed to be close to 0.5 for outer-sphere electrochemical reactions[11]). Equation (14) is therefore anticipated to yield more reliable values of ΔS^*_{int}, at least in the weak-interaction limit, since it circumvents the known severe limitations of the Born model for calculating static entropies.

The latter model is retained for estimating the optical component *in lieu* of any direct experimental information to the contrary. The justification for this approach is that the Born model is likely to be much more reliable for estimating the optical rather than the static component in view of the relative insensitivity of ε_{op} to solvent structure. Thus the extensive local perturbations in solvent structure induced around an ionic solute that are responsible for the failure of the dielectric continuum

model for predicting ionic solvation thermodynamics should have a much smaller influence on the intramolecular electronic perturbations which constitute the optical component of the reorganization barrier.

A comparison between values of ΔS^*_{int} calculated from Eqs. (13) and (14) for some representative redox couples in aqueous media is presented in Table I. Whereas the dielectric continuum model [Eq. (13)] predicts that ΔS^*_{int} will be small and largely independent of the chemical nature of the redox couple, somewhat larger and more varying values of ΔS^*_{int} are predicted by Eq. (14) since this takes into account specific reactant-solvent interactions via inclusion of the experimental values of ΔS°_{rc}. Further, the latter relation predicts markedly larger variations in ΔS^*_{int} with solvent than obtained with the former relation, resulting from the much greater sensitivity of ΔS°_{rc} to the solvent than predicted by the Born model.[16-18]

Although the differences between Eqs. (13) and (14) have been emphasized here, it should be noted that the ΔS^*_{int} values obtained by the latter are still relatively small. An interesting result is that for multicharged reactants very large thermodynamic solvation effects translate to much smaller intrinsic entropic barriers. For example, the $Fe(H_2O)_6^{3+/2+}$ self-exchange reaction involves thermodynamic entropy changes amounting to 360 J. deg^{-1} mol^{-1} (180 J deg^{-1} mol^{-1} for each half reaction)which yields an entropic contribution of just 13 J. deg^{-1} mol^{-1} to the Franck-Condon barrier (Table I). Still, the effects are large enough to warrant consideration. For example, for the $Fe(H_2O)_6^{3+/2+}$ reaction ΔS^*_{int} should contribute a factor of five to the self-exchange rate constant at room temperature. This effect is therefore comparable in magnitude to the nuclear tunneling corrections and nonadiabatic electron tunneling factors which have been emphasized in the recent literature.[2,21]

Comparisons with Experiment

In addition to the calculated values of ΔS^*_{int}, some "experimental" values for these homogeneous self-exchange reactions, ΔS^*_{int}(exp), are given in Table I. The latter were extracted from the measured activation enthalpies, ΔH^*, and the rate constants, k, using

$$k = K_p \Gamma_n \nu_n \exp(\Delta S^*_{int}/R) \exp(-\Delta H^*/RT) \qquad (15)$$

where K_p is the equilibrium constant for forming the precursor complex immediately prior to the electron-transfer step, Γ_n is the nuclear tunneling factor, and ν_n is the nuclear frequency factor.[2,21] {Note that the activation entropy in Eq. (15) can be directly identified with ΔS^*_{int} since $\Delta S^\circ = 0$ for self-exchange reactions [Eq.(1)]}. The values of K_p and ν_n were calculated as described in ref. 4. The values of ΔS^*_{int}(exp) were corrected for the variation of Γ_n with temperature by calculating this quantity using the relationships given in ref. 2.[22]

It is seen in Table I that the values of ΔS^*_{int}(exp) are uniformly smaller, i.e. more negative, than the estimates of ΔS^*_{int} from both Eq. (13) and Eq. (14). Such negative values of ΔS^*_{int}(exp) are commonly observed for homogeneous outer-sphere reactions.[23] They have been variously attributed to an unfavorable contribution to the precursor work term arising from reactant-solvent interactions, to the occurrence of nonadiabatic pathways, and to steric factors.[23,24] In any case, in view of the present discussion it appears likely that these negative values of ΔS^*_{int} reflect properties of the bimolecular precursor complex rather than those of the individual redox couples; i.e. reflect the modification of the solvation environment around each redox center brought about by its proximity to the coreactant necessary for electron transfer. In fact, the inclusion of specific

reactant-solvent interactions in the calculation of ΔS^*_{int} for the weak interaction limit by employing Eq (14) rather than Eq (13) leads in most cases to more positive values of ΔS^*_{int} (Table I).

Before accepting this conclusion, however, it is worth examining further the various assumptions embedded in Eq. (14). Given the breakdowns observed thus far in the Born solvation model, it is possible that the assumed quadratic variation of entropy with charge is also incorrect. The magnitude of the intrinsic activation entropy obtained from Eq. 14 is closely connected to the functional dependence of entropy on charge. For example a linear dependence leads to a value of zero for ΔS^*_{int}. Other functions might lead to large imbalances of forward and reverse entropic barriers and therefore substantial intrinsic activation entropies. Since most couples exhibit positive values of ΔS°_{rc} a fractional dependence of entropy on charge would normally be required to deduce negative values of ΔS^*_{int}. The entropy-charge relation was the subject of a number of detailed examinations and some controversy in previous years, and apparently was never unambiguously resolved.[25-27] One reason for this was the difficulty of varying the ionic charge while holding constant the other relevant parameters such as ionic size, ligand composition, coordination number, etc.

In order to determine the relation between entropy and charge for a prototype system we examined the reaction entropies of ruthenium tris bipyridine, for which oxidation states 0, I, II, and III are accessible in acetonitrile. The experimental details are given in ref. 16. By employing the same compound in various oxidation states the numerous complications and ambiguities inevitably involved in previous studies are avoided. The reaction entropies thus obtained for the $Ru(bpy)_3^{3+/2+}$, $Ru(bpy)_3^{2+/+}$, and $Ru(bpy)_3^{+/0}$ couples, respectively, in acetonitrile (containing 0.1 $\underline{M}$ KPF_6 supporting electrolyte)

are 117, 71 and 23 J deg^{-1} mol^{-1}. If these data are recast as relative single ion entropies, $\bar{S}° + K$, where K is an unknown constant quantity, a straightforward variation of entropy with the square of ionic charge is evident (Fig. 2), supporting the validity of Eq.(14).

It is possible of course that the ruthenium tris bipyridine reactions represent an atypical case. Another way of exploring the possibility that the negative experimental values of ΔS^*_{int} might arise in part from mismatches in the thermodynamic entropic changes occurring in each half reaction is to examine if the magnitude of ΔS^*_{int} depends on the sum of the constituent $\Delta S°_{rc}$ values. The larger these entropy changes, the larger should be the mismatch in ΔS^*_f and ΔS^*_r for each half reaction, yielding larger (or more negative) values of ΔS^*_{int}. However, such an examination for about thirty self-exchange and cross reactions shows no signs of such a systematic trend. (Details will be given elsewhere[5]). In addition, the experimental values of ΔS^*_{int} also show no discernable dependence on the magnitude of the reorganization barrier, comparable negative values of ΔS^*_{int} being obtained even for extremely rapid reactions.[5,23] This provides evidence that these negative values are associated either with an entropically unfavorable work term and/or nonadiabaticity, rather than residing in the elementary reorganization barrier to electron transfer of which the estimates of ΔS^*_{int} obtained from Eq. (14) form a part.

Nevertheless, the method of calculating ΔS^*_{int} embodied in Eq. (14) is considered to be useful since it provides a reliable estimate of ΔS^*_{int} for the limiting "weak interaction" case where the solvating environments of the two reactants do not modify each other, while accounting properly for the influence of the actual reactant-solvent interactions upon the entropic reorganization barrier for these isolated redox environments. It therefore

provides a more trustworthy means of gauging the extent of reactant-reactant interactions upon the activation entropy than is obtained by employing the conventional relationship [Eq. (13)], as well as supplying useful insight into the physical and chemical factors that determine this quantity.

A related approach to that described here can also be employed to estimate the effects of isolated reactant-solvent hydrogen bonding on the intrinsic enthalpic component of the Franck-Condon barrier. This involves examining the solvent dependence of the half-cell redox thermodynamics.[28] Preliminary results indicate that such enthalpic effects are markedly larger than the corresponding entropic factors examined here, contributing several $kJ. mol^{-1}$ to the intrinsic free energy barriers for a number of reactions.[28] These findings suggest that such specific reactant-solvent interactions may indeed account in part for the common observation that the experimental rate constants for homogeneous outer-sphere reactions are significantly smaller than the theoretical predictions where the outer-shell reorganization energy is calculated using the conventional dielectric continuum model.[4,5]

Acknowledgments

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Figure Captions

Fig. 1

Schematic representation of the ionic entropy of an individual redox center as a function of its effective ionic charge during the electron transfer step. See text for details.

Fig. 2

Plot of relative ionic entropy of $Ru(bpy)_3^n$ (bpy = 2,2'-bipyridine) in acetonitrile as a function of the square of the ionic charge n. The solid line is the best fit through the experimental points; the dashed line is the slope of this plot predicted by the Born model.

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TABLE I. Intrinsic Activation Entropies for Selected Homogeneous Self-Exchange Reactions, ΔS^*_{int} (J deg^{-1} mol^{-1}), calculated without (Eq. (13)) and with (Eq. (14)) Consideration of Specific Reactant-Solvent Interactions, and Comparison with Experiment.

Redox Couple	Solvent	r,Å,[a]	ΔS^*_{int} (Eq. 13)[b]	ΔS^*_{int} (Eq. 14)[c]	ΔS^*_{int} (experiment)[d]
$Fe(OH_2)_6^{3+/2+}$	H_2O	3.3	-1.5	13	-62
$V(OH_2)_6^{3+/2+}$	H_2O	3.3	-1.5	12.5	-61
$Ru(NH_3)_6^{3+/2+}$	H_2O	3.3	-1.5	2.5	-24 [e]
$Co(en)_3^{3+/2+}$ [f]	H_2O	4.2	-1.5	9.5	-45
$Ru(bpy)_3^{3+/2+}$ [g]	H_2O	6.7	-1.0	-4.5	--
ferricinium-ferrocene	H_2O	3.8	-1.5	-15	--
ferricinium-ferrocene	methanol	3.8	-6.5	-9.5	-44
ferricinium-ferrocene	nitromethane	3.8	-6.0	16	-29

Footnotes to Table I

[a]Reactant radius, used to calculate ΔS^*_{int} [Eq. 13]. Values taken from refs 4 and 18.

[b]Intrinsic activation entropy, calculated from Eq. (13) using the listed values of r and assuming that[4] $R_h = 2r$. Literature values of ε_s, $(d\varepsilon_s/dT)$, ε_{op}, $(d\varepsilon_{op}/dT)$: water-ε_s = 78.3, $(d\varepsilon_s/dT)$=-0.365, ε_{op}=1.78, $(d\varepsilon_{op}/dT)$=-0.00024, (values from "CRC Handbook for Chemistry and Physics", 56th ed., pp. E61, E224); methanol- ε_s=32.6, $(d\varepsilon_s/dT)$=-0.20, (Sears, P.G.; Holmes, R.R.; Dawson, L.R.; J. Electrochem. Soc., 1955, 102, 145); ε_{op}=1.76, $(d\varepsilon_{op}/dT)$=-0.0011, (Riddick, J.A.; Bunger, W.B., "Organic Solvents", Wiley-Interscience, New York, 1970, p. 145); nitromethane-ε_s=35.5, $(d\varepsilon_s/dT)$=-0.16, (Smyth, C.P.; Walls, W.S.; J. Chem. Phys., 1935, 3, 557); ε_{op}=1.90, $(d\varepsilon_{op}/dT)$=-0.0010, (Riddick, J.A.; Bunger, W.B.; op. cit., p. 391).

[c]Intrinsic activation entropy, calculated from Eq. (14) similarly to footnote b above, using the experimental values of ΔS°_{rc} taken from refs. 12 and 18.

[d]Values extracted from published rate data by using Eq. (15) and correcting for nuclear tunneling effects. Values of $K_p \nu_n$ are circa. 3×10^{12} M^{-1} s^{-1} (see refs. 4 and 5). Literature sources for rate data: $Fe(H_2O)_6^{3+/2+}$ - Silverman, J.; Dodson, R.W.; J. Phys. Chem., 1952, 56, 846; $V(H_2O)_6^{3+/2+}$ - Krishnamurty, K.V.; Wahl, A.C.; J. Am. Chem. Soc., 1958, 80, 5921; $Ru(NH_3)_6^{3+/2+}$ - Meyer, T.J.; Taube, H.; Inorg. Chem., 1968, 7, 2369; $Co(en)_3^{3+/2+}$ - Dwyer, F.P.; Sargeson, A.M.; J. Phys. Chem., 1961, 65, 1892; ferricinium/ferrocene - Yang, E.S.; Chan, M.S.; Wahl, A.C.; J. Phys. Chem., 1980, 84, 3094.

[e]Brown and Sutin (J. Am. Chem. Soc., 1979, 101, 883) have questioned the accuracy of this result, based on the more negative ΔS^* value for the $Ru(en)_3^{3+}$ - $Ru(NH_3)_6^{2+}$ cross reaction.

[f]en = ethylenediammine.

[g]bpy = 2,2'-bipyridine.

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